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Article

Visible-Light Amine Thioxanthone Derivatives as Photoredox Catalysts for Photopolymerization Processes

Emilia Hola, Paweł Fiedor, Andrzej Dzienia, and Joanna Ortyl*

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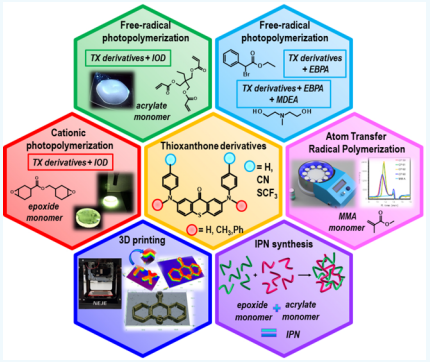
ABSTRACT: Herein, mono- and disubstituted thioxanthones have been synthesized and introduced as photosensitizers of iodonium salt for cationic and free-radical photopolymerization of epoxy and an acrylate monomer, respectively. Photoinitiation activity of these molecules was verified during photopolymerization processes performed upon exposure to visible LEDs of 420, 455, and 470 nm. The kinetics of the photopolymerization processes was followed using FT-IR spectroscopy. Moreover, the developed compounds were proposed as strongly reducing metal-free photoredox catalysts in organocatalyzed atom transfer radical polymerization (ATRP). Thioxanthone derivatives (with alkyl halide) efficiently activate the ATRP of methyl methacrylate using a visible LED as an irradiation source. The formed polymers in the ATRP process were characterized by SEC. Apart from studying the photopolymerization processes with the participation of obtained thioxanthones, absorption, fluorescence, as well as electrochemical properties of thioxanthone derivatives were investigated. Furthermore, the performance of studied compounds in 3D printing applications was also examined. The most important result of this study is the design and possible application of photosensitizers/photocatalysts for photopolymerization processes.



KEYWORDS: *thioxanthone, photopolymerization, sensitizer, cationic photopolymerization, free-radical photopolymerization, ATRP*

INTRODUCTION

Photochemistry has played an important role in polymer material science almost since its beginning.[1] Recently, visible-light-induced chemical reactions have attracted more and more attention due to their variable and mild reaction conditions.[2] The photopolymerization method is extremely popular as a way for production of polymers according to environmental and economic advantages.[3,4] Moreover, photodriven processes are gaining popularity as a safe method for production of polymers, which is relevant for green technology.[5,6]

Photopolymerization has found application in the coating industry, mainly in paints and varnishes, and in the furniture and automotive industries.[7,8] What is more, photoinduced processes are also used in many other industries, including in the printing industry, microelectronics, microlithography,[9] as well as in medicine[10] and dentistry.[11,12] Photopolymerization processes play also an influential role in 3D printing technologies,[13−15] SLA (stereolithography apparatus),[16] DLP (digital light processing),[17] and CLIP (continuous liquid interface production).[18] The vast majority of these applications use a unique and very important feature of photochemical initiation—spatial resolution, limiting the polymerization reaction only to the irradiated areas.[19]

Controlled radical polymerization (CRP), especially reversible deactivation radical polymerization (RDRP), has changed the science of polymer materials by empowering convenient synthesis of polymer materials characterized by precisely defined average molecular weights and architecture.[20] Obtaining polymers with the desired properties, i.e., molecular weight and low polydispersity, is particularly important when examining, among others, the physicochemical and rheological properties of polymers for the future application of these materials. CRP processes include a group of radical polymerization methods that are very popular due to the fact that they have provided simple routes to produce well-defined polymers as functional materials.

Among all the possibilities of controlled radical polymerization (CRP), atom transfer radical polymerization (ATRP) is perhaps the most extensively utilized method. Atom transfer radical polymerization is a great way to yield defined polymeric materials and (co)polymers with defined molecular weights and narrow polydispersity.[21]

Traditionally, ATRP required a high transition metal (e.g., Cu(I), Ru(II), Fe(II)) catalyst concentration in the presence of an appropriate ligand to generate propagating species.[22]

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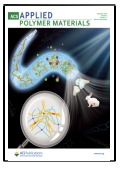
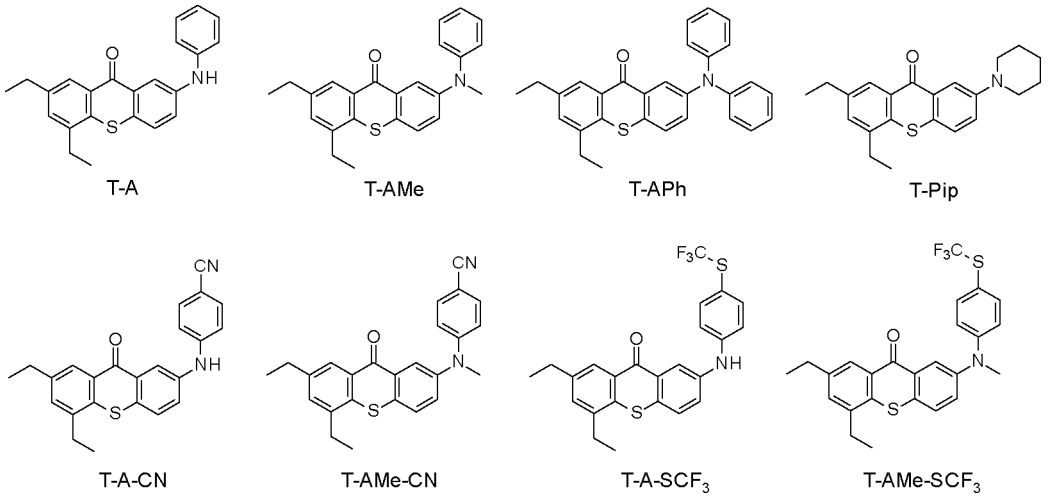


Scheme 1. Studied Thioxanthone Derivatives from Series 1



Copper-based ATRP (with a ppm concentration of Cu) was also reported in aqueous solutions using a light source from a visible region of light.[23] Photochemically induced ATRP with a low concentration (ppm) of copper catalysts was performed by the Matyjaszewski group using sunlight as a light source.[24]

The use of a metal-free variant of ATRP eliminates metal contamination in the polymer product that is undesirable for certain, for example, biomedical- and electronics-related applications.[25,26] Therefore, photoredox catalysis found application in photoinduced synthesis of polymer materials, performed in a control manner. It is possible by using strongly reducing organic photocatalysts, which are able to directly reduce activated alkyl bromide.[27]

A broad group of organic compounds, e.g., perylene,[28,29] phenothiazine and its derivatives,[25,30] diaryl dihydrophenazine,[26,31] thienothiophene derivatives,[32] phenoxazine,[33] carbazole derivatives,[34] and 1,1′-bisnaphthol[35] were reported for the role of photocatalysts for photopolymerization of a methyl methacrylate monomer. These compounds enable atom transfer radical polymerization under UV irradiation or visible light. There is no doubt that an appropriate organic photocatalyst is the most important factor to reach an efficacious metal-free ATRP catalytic system.

What is also important is the light source that is used for photoinduced processes. Lately, *light-emitting diodes* (LEDs) have become more and more popular as a light sources for photodriven polymerization processes.[36] Curing with LEDs is one of the most popular trends in coating technology today. The technology of LED diodes is also known according to rapid evolution. Proficiency and environmental profits are the most important attributes in this case.[37,38]

Thioxanthone, which belongs to typical example of commercially available type II photoinitiators and acts in combination with an appropriate coinitiator, is also a popular organic compound in photochemistry.[39] What is more, the thioxanthone molecule is a well-known photosensitizer[40] that is applied for photopolymerization processes.[41,42] A few years ago, Allushi et al. investigated also thioxanthone and 2-isopropylthioxanthone together with amine *N,N,N′,N″,N‴*-pentamethyl-diethylenetriamine (PMDETA) and alkyl halides in atom transfer radical polymerization.[43]

In this work, synthesis of structurally modified thioxanthone-based compounds was performed in order to obtain active components for two- and three-component photoinitiator systems for cationic and free-radical polymerization performed upon exposure to visible light. Our goal was to test how the substitution of 7-bromo-2,4-diethyl-thioxanthen-9-one and double substitution of 2,7-dibromothioxanthen-9-one with an amino moiety would affect their properties, in particular, the absorption properties, electrochemical properties, and efficiency in photoinitiating systems. In the next step, it was checked how the introduction of aromatic amines, aniline, and aniline with various substituents in the *para*-position (electron-donating group, $-SCF_3$, and electron-withdrawing group, $-CN$) would differentiate the properties of the synthesized compounds. Sequentially, a methyl moiety was introduced into the $-NH$ group of studied compounds to obtain tertiary amines. For compounds with aniline, a phenyl moiety was also introduced to check the difference between methyl and phenyl substituents. Finally, the aliphatic amine piperidine was added to the thioxanthone basic cores.

Developed thioxanthone derivatives are also proposed to be high-performance organic metal-free photocatalysts dedicated to photoinduced atom transfer radical polymerization.

EXPERIMENTAL SECTION

Materials. A total of 16 compounds, thioxanthen-9-one derivatives, were studied as photosensitizers of iodonium salt in two-component photoinitiator systems, series 1: 7-anilino-2,4-diethyl-thioxanthen-9-one (T-A), 2,4-diethyl-7-(*N*-methylanilino)thioxanthen-9-one (T-AMe), 2,4-diethyl-7-(*N*-phenylanilino)thioxanthen-9-one (T-APh), 4-[(5,7-diethyl-9-oxo-thioxanthen-2-yl)amino]-benzonitrile (T-A-CN), 4-[(5,7-diethyl-9-oxo-thioxanthen-2-yl)-methylamino]benzonitrile (T-AMe-CN), 2,4-diethyl-7-[4-(trifluoromethylsulfanyl)anilino]thioxanthen-9-one (T-A-SCF_3), 2,4-diethyl-7-[*N*-methyl-4-(trifluoromethylsulfanyl)anilino]thioxanthen-9-one (T-AMe-SCF_3), 2,4-diethyl-7-(1-piperidyl)thioxanthen-9-one (T-Pip); and series 2: 2,7-dianilinothioxanthen-9-one (T-bisA), 2,7-bis(*N*-methylanilino)thioxanthen-9-one (T-bis(AMe)), 2,7-bis(*N*-phenylanilino)thioxanthen-9-one (T-bis(APh)), 4-[[7-(4-cyanoanilino)-9-oxo-thioxanthen-2-yl]amino]benzonitrile (T-bis(A-CN)), 4-[[7-(4-cyano-*N*-methyl-anilino)-9-oxo-thioxanthen-2-yl]-methylamino]-benzonitrile (T-bis(AMe-CN)), 2,7-bis[4(trifluoromethylsulfanyl)-anilino]thioxanthen-9-one (T-bis(A-SCF_3)), 2,7-bis[*N*-methyl-4-(trifluoromethylsulfanyl)anilino]thioxanthen-9-one (T-bis(AMe-SCF_3)), and 2,7-bis(1-piperidyl)thioxanthen-9-one (T-bis(Pip)). Details for the syntheses and data of the TX derivatives are available

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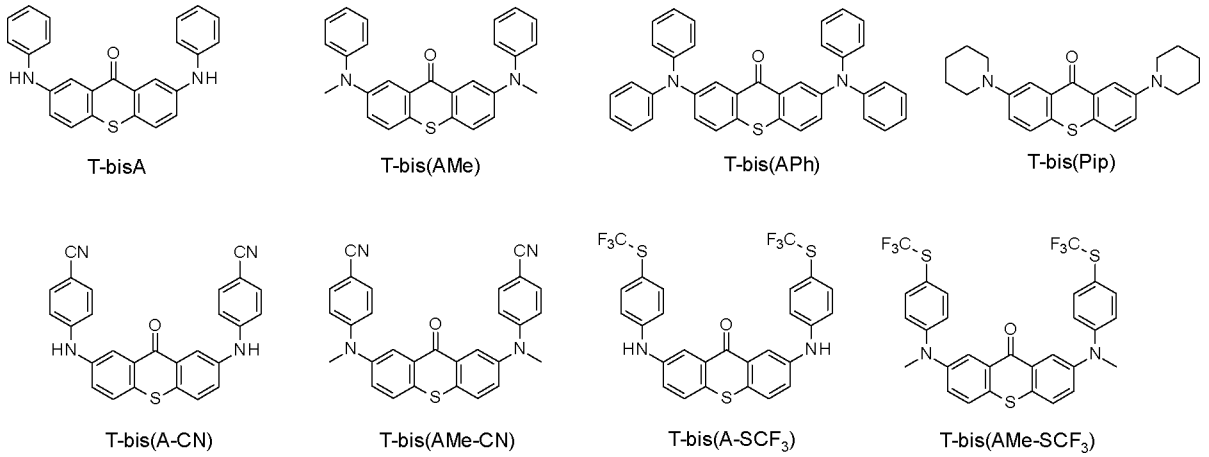
Scheme 2. Studied Thioxanthone Derivatives from Series 2



in the Supporting Information. The chemical structures of investigated molecules are presented in Schemes 1 and 2.

Chemicals Used for Experimental Work. Monomers of different chemical compounds applied for proposed experiments were used with the best accessible purity. As an epoxy monomer, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (UVACURE1500, from Allnex) was utilized. Bis(4-*t*-butylphenyl)-iodonium hexafluorophosphate (IOD - Speedcure 938, from Lambson Ltd., UK) was exploited as a cationic initiator. As an acrylate, trimethylopropane triacrylate (TMPTA, from Sigma-Aldrich) was applied. Methyl methacrylate (from Sigma-Aldrich) was used for the ATRP reaction. *N*-Methyldiethanolamine (MDEA) and ethyl α-bromophenylacetate (EBPA), *N*,*N*-dimethylformamide for HPLC (DMF), and lithium bromide were purchased from Merck, previously Sigma-Aldrich. Thioxanthen-9-one (TX) (from TCI) and 2,4-diethyl-9*H*-thioxanthen-9-one (DETX) (from Sigma-Aldrich) were used as references.

Instrumentation—General Methods. *Recording of Absorption Spectra.* A Silver Nova spectrometer was applied to record the absorption spectra of derivatives of thioxanthone in acetonitrile.

Recording of Excitation and Emission Spectra. Fluorescence emission and excitation spectra were registered with a Quanta Master 40 (from Horiba) spectrofluorometer as described in our previous papers.[41,44]

Fluorescence quenching studies of thioxanthen-9-one derivatives were carried out using the same spectrofluorometer and procedure described in detail elsewhere.[44]

Method of Determining Oxidation and Reduction Potentials. The oxidation and reduction potentials (E_{ox} and E_{red} vs silver/silver chloride electrode) of the investigated TX derivatives were studied using acetonitrile as a solvent by cyclic voltammetry.[41] Values of ΔG_{et} for an electron-transfer process between a photoinitiator (iodonium salt) and sensitizer were estimated based on the Rehm−Weller equation.[45]

Size Exclusion Chromatography. Molecular weights and dispersities were designated using SEC, a Viscotek GPC Max VE 2001 instrument, and a Viscotek TDA 305 triple-detection instrument (refractometer, viscosimeter, and low-angle laser/right-angle light scattering) utilized for data collecting and an OmniSec 5.12 for data processing. One D6000 M general mixed bead column was used for separation. DMF of HPLC purity (Merck) was applied as a solvent at 323.15 K at a flow rate of 0.7 mL·min^{-1}. The addition of 10 mM lithium bromide (Merck) was used to reduce the interactions between the polymer and the column. The apparatus was appplied in triple-detection mode. For determination of absolute values of molar mass (M_n and M_w) and the dispersities ($Đ$), triple detection was used (with calibration with a narrow poly(methyl methacrylate) standard). The dn/dc value for the final analysis of macromolecular parameters was estimated from the average of several analyses of the obtained polymers and was chosen as dn/dc = 0.057 mL·g^{-1}.[46]

Photopolymerization Processes. Bimolecular photoinitiating systems containing iodonium salt (IOD, concentration 1.0%, 1.9 × 10^{-2} mol·dm^{-3}) and thioxanthen-9-one-based compounds (concentration 2.8 × 10^{-3} mol·dm^{-3}) were applied for photopolymerization reactions.

Kinetics of photopolymerization processes as well as a final conversion of monomers were determined based on studies conducted with application of a real-time FT-IR spectrometer (Nicolet iS10, from Thermo Scientific U.S.). A detailed procedure for conducting cationic, free-radical polymerization and IPN synthesis was reported in our previous paper.[41]

Light Sources. The sources of light used in experiments were LEDs (from Thorlabs Inc.) of 420 nm (M420L3), 455 nm (M455L3), and 470 nm (M470L3), and as a power supply, DC2200 (from Thorlabs Inc.) was utilized. The diode was turned on 10 s after the starting of the registration FT-IR spectra. The sample was placed 2.1 cm from the light source. The appropriate light intensities at the sample surface were calculated and were equal to 14.87 mW·cm^{-2} for vis-LED @ 420 nm, 17.84 mW·cm^{-2} for vis-LED @ 455 nm, and 12.88 mW·cm^{-2} for vis-LED @ 470 nm.

Photo-ATRP Process. The atom transfer radical polymerization (photo-ATRP) of methyl methacrylate (MMA) was carried out in the presence of the alkyl bromide, ethyl α-bromophenylacetate (EBPA, 0.06 mmol, 1 equiv), and a catalyst, a derivative of thioxanthone (0.01 mmol, 0.1 eq), using dimethylacetamide as a solvent ($V_{MMA} = V_{DMAc}$) under an inert atmosphere, argon. The composition with a magnetic stirring bar was sealed in a vial and placed in photoreactor (from Photo4Chem Ltd.) for 4 h (irradiation with an LED @ 405 nm—an intensity of approximately 54 mW·cm^{-2}, measured using optical power meter PM160 from Thorlabs).

Multistation Modular Photochemical Reactor for ATRP Process. A photochemical reactor used for ATRP processes is a device (Figure 1) specially designed and manufactured for use in R&D by Photo4Chem Ltd. (Cracow, Poland). Thanks to the use of a multistation, replaceable rotor, adapted to work with various sizes of reaction vessels, the photoreactor allows many photochemical processes to be carried out under the same lighting and temperature conditions. The design of the reactor also allows the use of a magnetic stirrer for continuous homogenization of the reaction systems. The modular design of the reactor allows for adjustment of the wavelength of light in the range of 254−1064 nm and enables work with reaction vessels with a size from 1 to 50 cm^3. The fully digital control system allows modification of all important operational parameters of the system, such as the wavelength of light, lighting power, and rotor speed. The reactor is controlled from the control panel located on the reactor housing or from the level of the computer application. The use of LED technology, in conjunction with a digital control system, minimizes the energy demand of the reactor, making it not only user-friendly but also environmentally friendly.

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Figure 1. Reactor design model and photo of the reactor.

3D Printing Experiment. An NEJE DK-8-KZ 1000 mW Laser Engraver Printer was applied for 3D printing experiments.

This device was equipped with a laser diode at 405 nm (intensity = 100 mW·cm^{-2}). The mixture of monomers with an appropriate initiating system (resin) was placed onto a microscope slide with a form stuck on it and was polymerized under air. The objects obtained after printing were analyzed by numerical optical microscope DSX1000 from OLYMPUS.

RESULTS AND DISCUSSION

Absorption Properties of Thioxanthen-9-one Derivatives. Chemical modification of the thioxanthone skeleton was done to increase the photosensitivity of these compounds in the visible region by introducing an amino-derivative group. The UV−vis absorption spectra of DETX and TX derivatives are presented in Figure 2; spectroscopic details, absorption maximum values, and values of molar extinction coefficients are summarized in Table S1 in the Supporting Information. Studied molecules are characterized by high molar extinction coefficients. Particularly, the absorption of thioxanthen-9-one-based compounds is observed in the visible range (400−500 nm), matching the emission characteristics of the vis-LEDs at 420 nm, 455 and 470 nm.

What is really important is that absorption spectra of investigated compounds are significantly shifted toward longer wavelengths in comparison to commercially used sensitizers: TX and DETX. The introduction of amine substituents evidently causes a bathochromic shift compared to TX and DETX. What is more, a decrease of molar extinction coefficients for long-wavelength absorption maximum is also observed. Modification of DETX or TX cores by introduction of an amine moiety has a clear influence on the absorption properties of synthesized structures in visible region.

Performance of the Thioxanthen-9-one-Based Compounds as Photosensitizers for Two-Component Photoinitiation Systems for Cationic Polymerization. The interest in cationic photopolymerization is continuously growing according to the applications in many areas of industry. The onium salts are known as popular photoinitiators used in cationic photopolymerization processes, e.g., iodonium salt bis(4-*t*-butylphenyl)-iodonium hexafluorophosphate) (IOD) and sulfonium salt triarylsulfonium hexafluorophosphate (TAS). The main disadvantage of these initiators is their absorption characteristics (IOD absorbs up to 320 nm, TAS absorbs up to 360 nm),[41] which makes them impossible to apply to processes that occur under the influence of visible light. As a solution to this problem, the thioxanthone derivatives have been proposed as photosensitizers of iodonium salt (IOD) in two-component initiating systems, thereby enabling photoinitiation of the polymerization with visible-light irradiation using vis-LEDs—420, 455, and 470 nm.

Cationic photopolymerization experiments via real-time FT-IR were performed for an epoxy monomer (UVACURE1500) in order to investigate how the structure of a photosensitizer impacts the photoinitiation efficiency in two-component photoinitiating systems. The light sources used in this experiment were adjusted to absorption characteristics of thioxanthone derivatives, light-emitting diodes (LEDs, 420, 455, and 470 nm). As references, DETX and TX were used under the same conditions. Final bond conversions of epoxy monomer after exposure to radiation for 800 s are summarized as histograms presented in Figure 3A,B for photosensitizers from series 1 and 2, respectively. Kinetic profiles (conversion vs time) are given in the Supporting Information (Figures S33

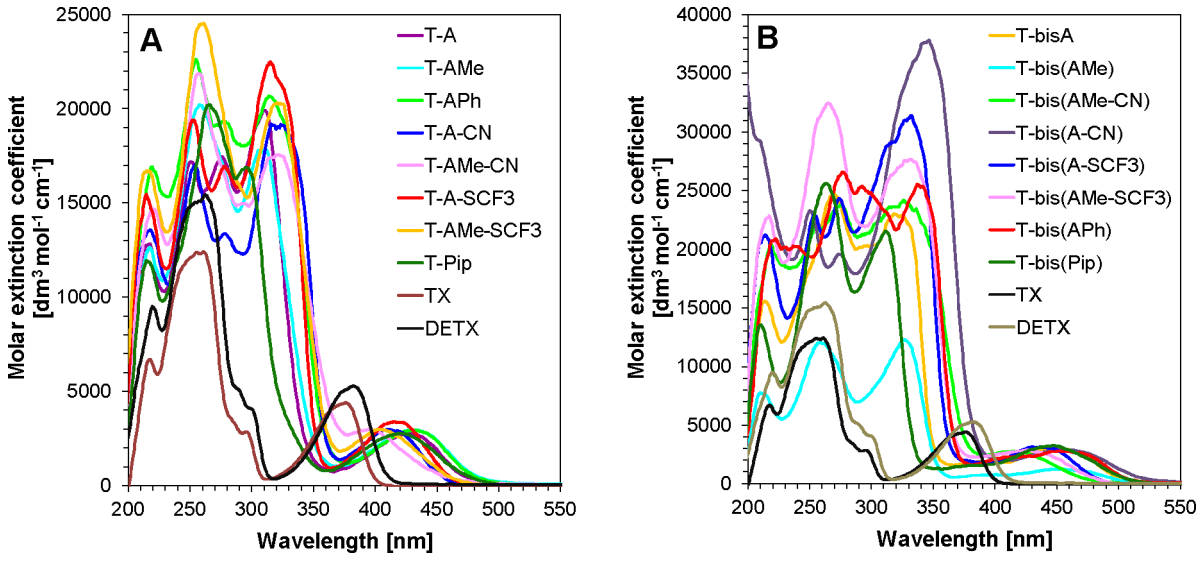

Figure 2. Absorption spectra of compounds (A) from series 1 and (B) from series 2 recorded using acetonitrile as a solvent.

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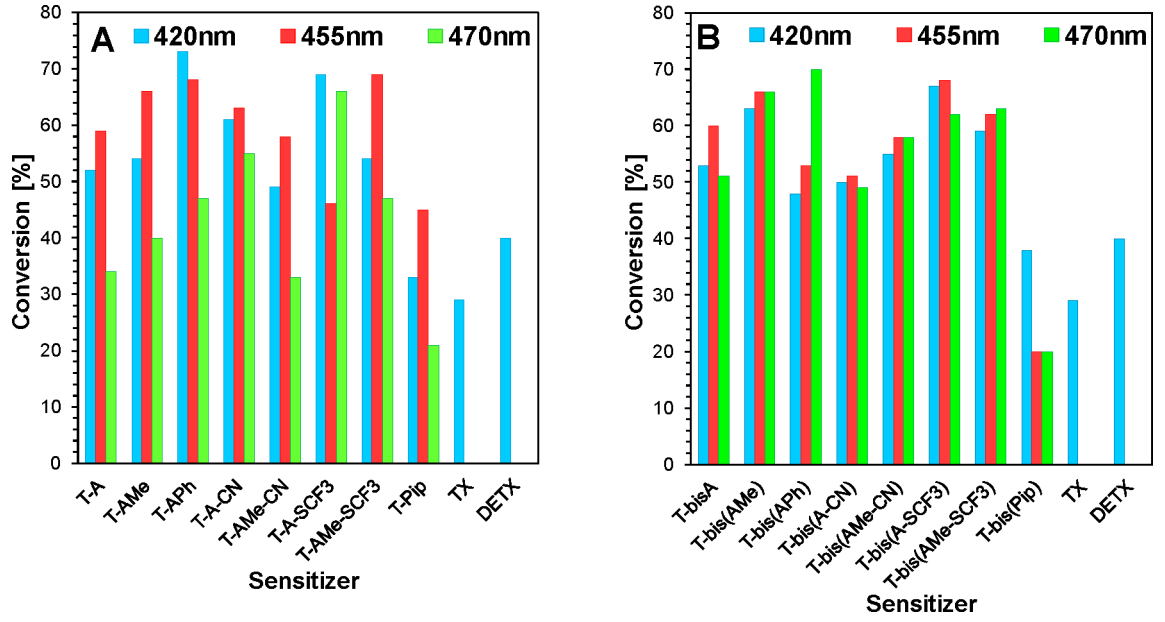

Figure 3. Conversion of UVACURE1500 after 800 s of irradiation with LEDs at 420, 455, and 470 nm under air, using studied initiating systems based on IOD (1% w/w) and derivatives of thioxanthenone (0.1 wt %) from (A) series 1 and (B) series 2.

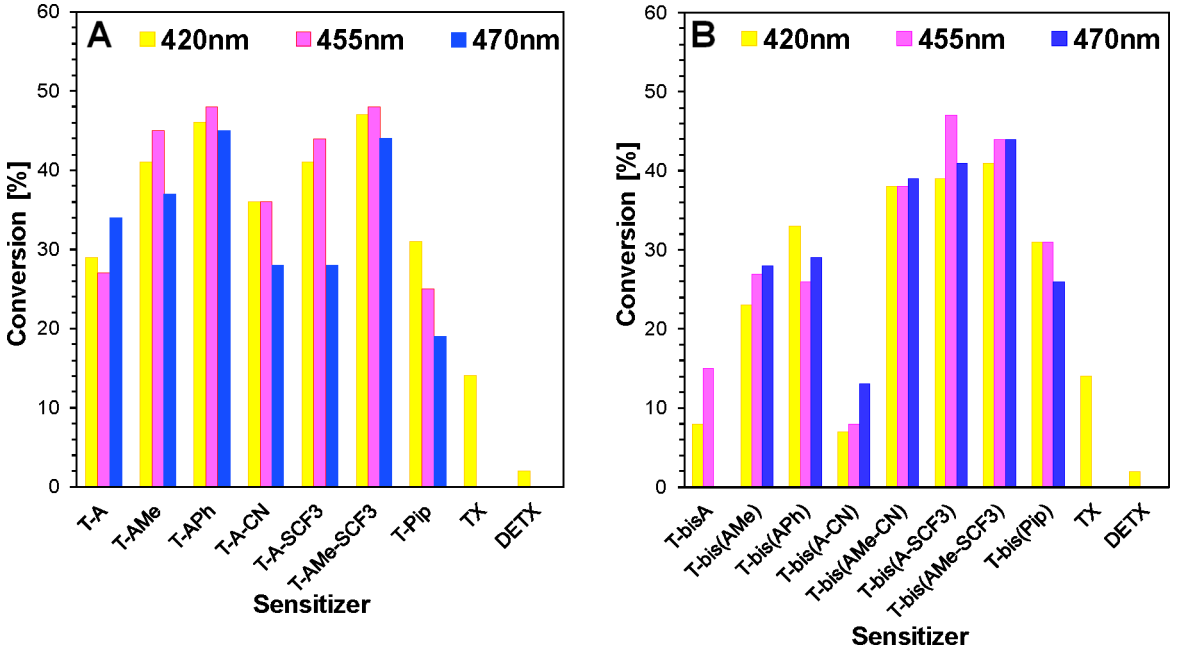

Figure 4. Conversion of TMPTA after 400 s of irradiation with LEDs at 420, 455, and 470 nm in laminate using an investigated initiating system containing IOD (1% w/w) and derivatives of thioxanthenone (0.1 wt %) from (A) series 1 and (B) series 2.

– S38), and data are also listed in Table S1 in the Supporting Information. There is no polymerization with iodonium salt (IOD) without any additive in studied conditions. Investigated bimolecular initiating systems are efficient in photopolymerization of epoxy monomer. Almost all systems exhibit better photoinitiating efficiency under an LED of 420 nm than commercially used TX and DETX. Upon exposure to LEDs of 455 and 470 nm, all systems are better, according to the fact that photopolymerization in the presence of TX/IOD and DETX/IOD does not occur. It is associated with limited absorption properties of TX and DETX.

The best initiating performance (rate of polymerization and conversion) in cationic photopolymerization is observed for T-APh/IOD, T-A-SCF_3/IOD, and T-A-CN/IOD under an LED of 420 nm, for T-AMe-SCF_3/IOD, T-APh/IOD, and T-AMe upon irradiation with an LED of 455 nm, and T-A-SCF_3 and T-A-CN under an LED of 470 nm.

In some cases, the performance of thioxanthone derivatives from series 2 is similar to compounds from series 1 (for T-A-CN and T-bis(A-CN), T-AMe-CN and T-bis(AMe-CN), T-A-SCF_3 and T-bis(A-SCF_3), and T-Pip and T-bis(Pip). For the rest of the sensitizers, bisubstituted derivatives have better photoinitiation efficiency than monosubstituted derivatives.

Performance of the Thioxanthen-9-one-Based Compounds as Photosensitizers in Two-Component Initiating Systems for Free-Radical Photopolymerization of

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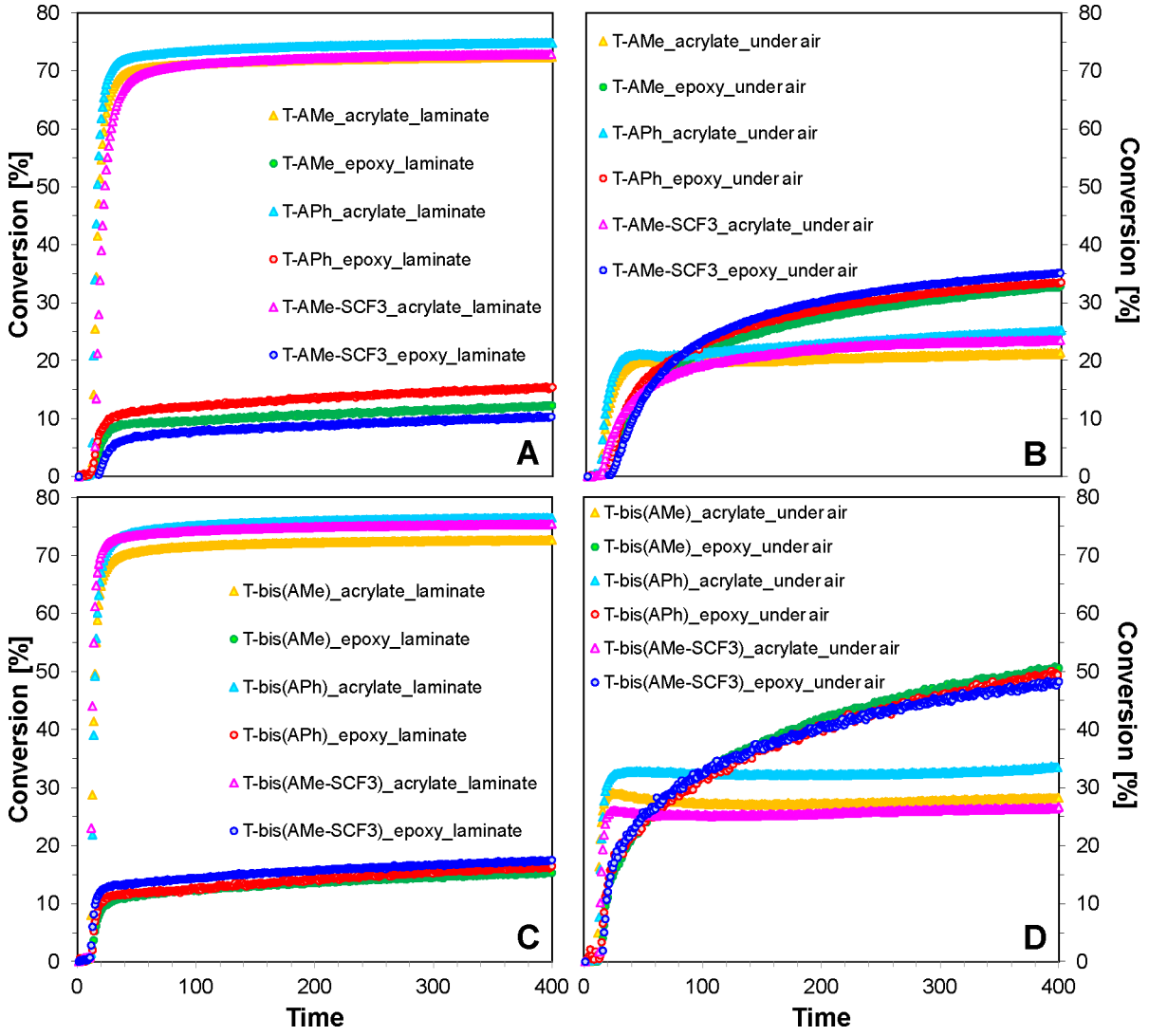

Figure 5. Polymerization profiles of acrylate and epoxy monomer (1:1 w/w) for IPN synthesis upon exposure to an LED at 455 nm in the laminate (A,C) or under air (B,D), using IOD (1% w/w) and derivatives of thioxanthenone (0.1% w/w) from series 1 (A,B) and from series 2 (C,D). The irradiation starts at t = 10 s.

Acrylates in Thin Films (Laminate). Thioxanthone with different amine substituents is also a powerful photosensitizer of iodonium salt in two-component initiating systems for free-radical photopolymerization of a TMPTA monomer. Light sources from the visible range have been selected, the same as for cationic photopolymerization with LEDs of 420, 455, and 470 nm. Results are presented as histograms in Figure 4A,B as well as in the Supporting Information (kinetic profiles, conversion vs time curves, Figures S39−S44, values of final conversion are summarized in Table S2 in Supporting Information). Compounds T-AMe-SCF$_3$, T-A-Ph, and T-AMe from series 1 exhibit the best ability to sensitize iodonium salt, and final acrylate conversion values are the highest for these systems. For derivatives from series 2, final conversions for formulations containing T-bis(AMe-CN), T-bis(A-SCF$_3$), and T-bis(AMe-SCF$_3$) have reached the highest values.

Performance of TX Derivatives as Photosensitizers for Synthesis of Interpenetrated Polymer Networks (IPNs). According to successful photopolymerization processes of an epoxy monomer as well as an acrylate monomer with initiating systems based on thioxanthone compounds and onium salt, IOD, synthesis of interpenetrated polymer networks (IPNs) was performed. The studied systems containing IOD and thioxanthone-based compounds were applied to induce cationic and radical polymerization of a mixture of epoxy monomer (UVACURE1500) and acrylate monomer (TMPTA) (50/50% w/w). Hybrid photopolymerization was performed under air and also in thin films upon exposure to a 455 nm vis-diode. Kinetic profiles for selected sensitizers from series 1 and 2 are shown in Figure 5A−D. Higher conversion was observed for an acrylate monomer in the laminate. The opposite situation took place for the epoxy monomer; higher conversion was observed for polymerization performed on the BaF_2 pellet under air. During photopolymerization in thin film, oxygen inhibition is limited, and that is why polymerization of an acrylate monomer is faster than that of an epoxy monomer.

3D Printing Experiment. 3D printing attempts realized under laser diode irradiation at 405 nm were implemented under air. Two-component initiating systems consisted of T-AMe, T-APh, T-AMe-SCF$_3$, T-bis(AMe), and iodonium salt in

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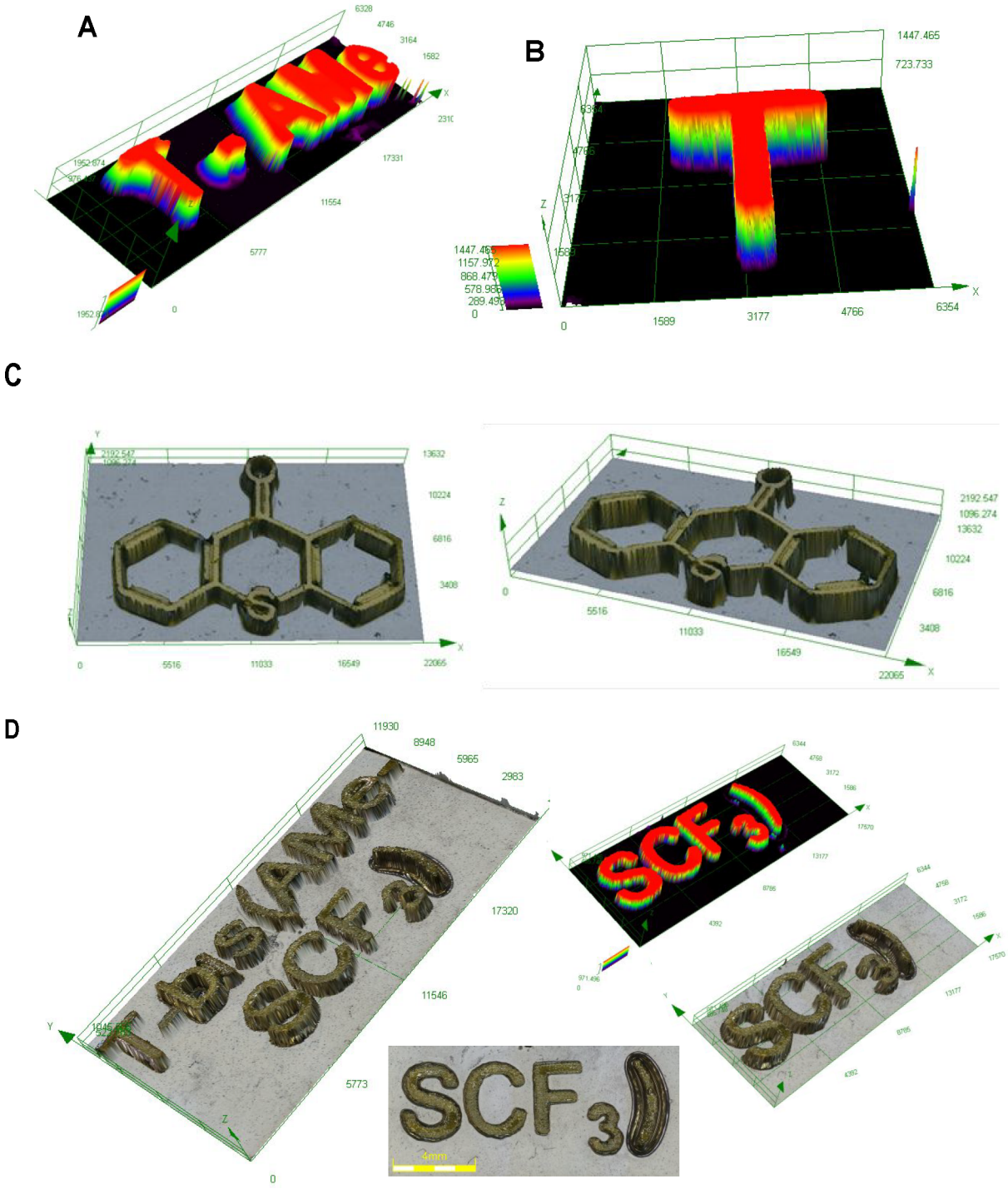

Figure 6. Samples produced in 3D printing experiment using TMPTA/UVACURE1500 (1:1) resin with (A) T-AMe (0.05% wt.)/IOD (1% wt.), thickness = 1952 μm, (B) T-APh (0.05% wt.)/IOD (1% wt.), thickness = 1447 μm, (C) T-AMe(0.05% wt.)/IOD (1% wt.), thickness = 2192.5 μm, (D) T-bis(AMe-SCF_3) (0.05% wt.)/IOD (1% wt.), thickness = 971 μm.

a mixture of TMPTA/UVACURE1500 monomers. Initiating systems based on all investigated derivatives of thioxanthone added for mixture of monomers enable efficient photopolymerization in the irradiated area. What is very important is that produced samples were characterized by high spatial resolution. The patterns were analyzed microscopically; examples are shown in Figure 6A–D.

Performance of the TX Derivatives as Photocatalysts in the Presence of Bromide for Free-Radical Photopolymerization. Studied thioxanthone derivatives were investigated as ingredients of two-compponent initiating systems in combination with bromide EBPA for photopolymerization of an acrylate monomer (TMPTA) using an LED of 420 nm. Final conversion results are presented in Figure 7A,B for compounds from series 1 and 2, respectively (conversion vs time profiles are presented in the Figures S45 and S46 in the Supporting Information, conversion values are summarized in Table S1 in the Supporting Information). All

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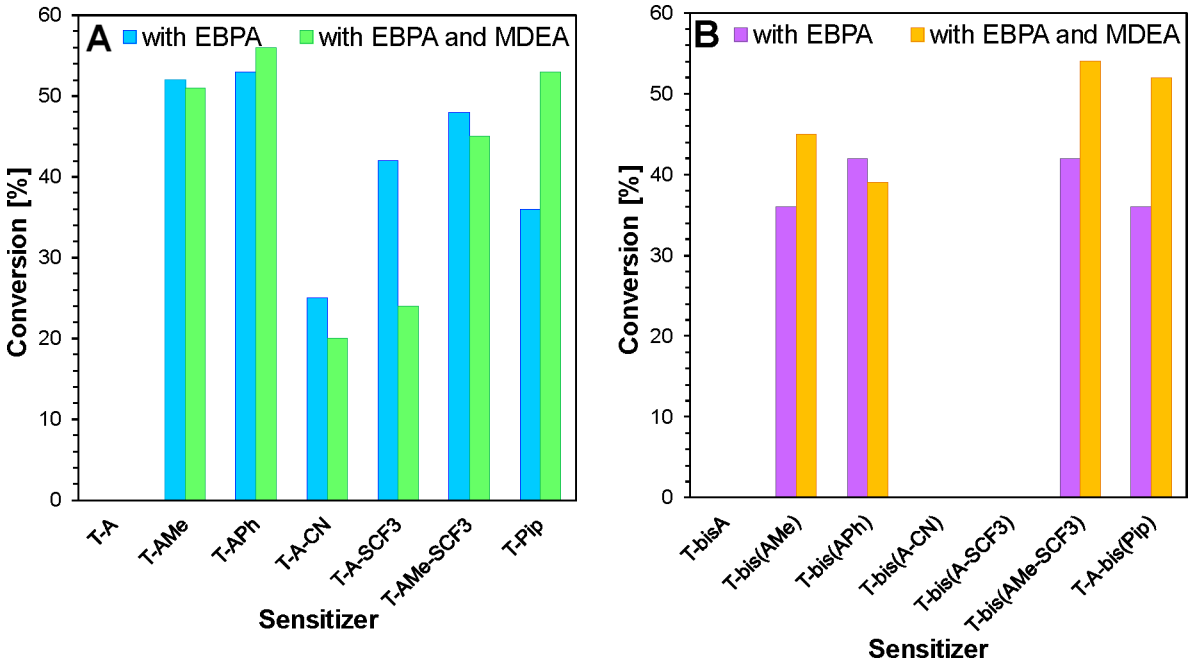

Figure 7. Conversion of TMPTA after 400 s of irradiation with an LED at 420 nm using studied initiating systems based on derivatives of thioxanthen-9-one (0.1 wt %) from (A) series 1 and (B) series 2 with EBPA (1.5% w/w) or with EBPA (1.5% w/w) and MDEA (1.5%).

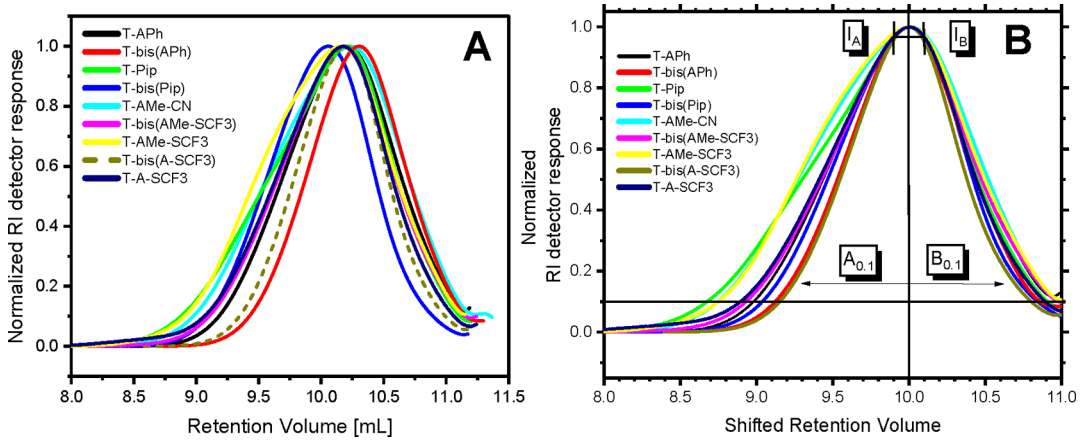

Figure 8. (A) Normalized refractive index detector response. (B) Comparison of the normalized shape of the peaks after peak alignment at the peak maximum and measurement of the asymmetry coefficient at an intensity of 0.1 from baseline.

monosubstituted thioxanthones are efficient in bimolecular initiating systems except one. Compound T-A in conjunction with bromide does not initiate photopolymerization of an acrylate monomer. The efficiency of derivatives T-A-CN and T-A-SCF_3 is rather weak; we can observe a long induction time in a kinetic profile (Figure S45). The most effective are T-AMe and T-APh; the final conversion of the acrylate monomer is around 50%, and the induction time is rather short for these two compounds. It can be concluded that compounds with an −NH moiety (secondary amine) are not efficient with bromide in photoinitiating systems (no polymerization for T-A, long induction time for T-A-CN and T-A-SCF_3). Compounds containing a tertiary amine in their structure (substituted −NH group) exhibit a high efficiency.

Photoinitiating systems containing catalysts from series 2 exhibit lower efficiency in comparison to derivatives from series 1 (final conversion values around 35−45%). Only disubstituted thioxanthone derivatives with a tertiary amine moiety are efficient and shows remarkably good conversion. Compounds with a secondary amine (T-bisA, T-bis(A-CN), T-bis(A-SCF_3)) do not initiate photopolymerization of an acrylate monomer in the presence of bromide EBPA. The most effective is T-bis(AMe-SCF_3); we can observe the shortest induction time in profiles presented in Figure S46, and the final conversion equals 42%.

Performance of TX Derivatives as Photocatalysts in Three-Component Initiating Systems in the Presence of Bromide and Amine for Free-Radical Photopolymerization. Thioxanthone derivatives were also investigated as photocatalysts in three-component initiating systems in conjunction with bromide (EBPA) and amine (MDEA) for free-radical polymerization of an acrylate monomer. In studied systems, the role of the amine is to react with the oxidized TX to regenerate the initial state photosensitizer. The interaction of the excited states of TX derivatives with bromide is more favorable than the interactivity with an amine. Final conversion

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results are presented as histograms in Figure 7 (conversion vs time profiles are presented in the Supporting Information, Figures S47 and S48, and summarized in Table S3). Final conversion values for two- and three-component photoinitiating systems with derivatives from series 1 are similar. Nevertheless, it can be seen that addition of amine resulted in a shorter induction time compared to the two-component system. For thioxanthones from series 2, addition of amine also caused a shorter induction time, and the final conversion values are higher for systems with bromide and amine.

Photoinduced Metal-Free Atom Transfer Radical Polymerization with Thioxanthone-Based Photocatalysts. To investigate the activity of the developed mono- (series 1) and disubstituted (series 2) thioxanthene derivatives in controlled radical photopolymerization, a model reaction of methyl methacrylate photopolymerization using the ATRP mechanism was carried out. The resulting polymers were analyzed using triple-detection gel permeation chromatography to determine the absolute, number-average M_n molecular weights and dispersity index. The raw data obtained from the refractive index detector were placed in the Supporting Information, Figure S49. To present the shape of the peaks in a consistent way, the data from the refractive index detector were normalized (Figure 8A). Analysis of reported data reveals that, independently of the catalyst used, the polymers weight distributions are monomodal; however, they differ significantly in the calculated dispersity index. Especially noteworthy is the dispersity of 1.15 achieved for T-bis(A-SCF_3), which allows relatively high molecular weights of M_n = 29.1 kg/mol to be obtained. Moderate dispersity values around $Đ$ = 1.4 were achieved also for the second of the catalysts with a secondary amine group and SCF_3 substituent, which is T-A-SCF_3. Similar results were reached for the T-bis(Pip) catalyst. Both of the above-mentioned disubstituted catalysts showed good activity in the previously discussed free-radical polymerization of TMPTA. Also worth mentioning is the activity provided by APh substitution, both for series I and II of thioxanthone, which yields polymers with dispersities of approximately 1.6. On the other hand, the methyl substituent at the amine definitely deteriorates the performance of the obtained polymers, which is well-demonstrated for T-AMe-CN, T-AMe-SCF_3, and T-bis(AMe-SCF_3).

Additionally, in order to parametrize the shape of the GPC peak derived from the synthesized polymers, the authors adopted the asymmetry factor, which is one of the parameters commonly used in other chromatographic methods, e.g., HPLC. This factor analyzes the ratio of the peak width at 10% peak height from baseline. The asymmetry factor, which is the ratio of the $A_{0.1}$ to $B_{0.1}$ peak width at 0.1 from the baseline, 0.[47] It is sensitive to changes in the distribution of molecular weights with respect to time or elution volume. Such a scenario may arise from perturbations in the kinetics of the polymerization process and cause, in addition to an overall broadening of the peak, a shift in the molecular weight distribution toward lower or higher molecular weights, resulting in deviations from the normal (Gaussian) molecular weight distribution.[48] The purpose of using shape parameters from other chromatographic methods to analyze the shape of the GPC peak is based on one main assumption. If the molecular weights of the analyzed polymer are within the linear range of separation, i.e., the linear part of the calibration curve, which has been determined for a given system after taking into account the type of employed columns, then the shape of the peak originating from the monodisperse polymer is well-described by a Gaussian distribution and the peak is fully symmetrical.[49] This assumption is fulfilled when there are no existing problems with the separation process that could contribute to artificial disruption or broadening of the peak shape, e.g., no interactions between the polymer and the column system, no dead volumes, and an adequate flow rate and sample loading.[49]

Table 1. Results for Polymers Obtained by Photoinduced Metal-Free ATRP Using Thioxanthone-Based Photocatalysts[a]

catalyst	M_n [kg/mol][b]	M_w [kg/mol][b]	$Đ$[b]	$A_{0.1}/B_{0.1}$[c]	conversion [%][d]
T-APh	16.2	25.9	1.60	1.07	23
T-bis(APh)	14.0	23.0	1.64	1.02	29
T-Pip	21.5	39.6	1.84	1.45	20
T-bis(Pip)	24.2	35.1	1.45	1.14	18
T-AMe-CN	15.0	31.9	2.13	1.30	33
T-AMe-SCF_3	19.7	39.6	2.01	1.28	24
T-bis(AMe-SCF_3)	17.9	31.5	1.76	1.11	27
T-A-SCF_3	30.5	43.8	1.43	1.23	22
T-bis(A-SCF_3)	29.1	33.3	1.15	1.06	15

[a]Reaction conditions: EBPA/MMA/CAT: 1:100:0.1, $V_{MMA} = V_{DMAc}$, LED = 405 nm, I = 54, 2 mW·cm^{-2}, time = 4 h. [b]M_n, M_w, and dispersity ($Đ$) were measured using SEC (DMF as eluent) calibrated to the poly(methyl methacrylate) standard. [c]$A_{0.1}/B_{0.1}$ asymmetry coefficient. [d]Determined gravimetrically.

Analysis of the results presented in Figure 8B reveals that in most cases the dispersity of the analyzed polymers correlates with the asymmetry factor. It means that for polymers with low dispersity, the asymmetry factor is close to unity, which means a symmetric peak, and with increasing dispersity, this factor increases to a value around 2. This involves a clear loss of control of the polymerization process in the high-molecular-weight region for some of the investigated catalysts. For the best of the catalysts, i.e., T-bis(A-SCF_3), this factor is equal to 1.06 at a dispersity of 1.15, while for other moderately good catalysts, the values range from 1.02 for T-bis(APh) to 1.23 for T-A-SCF_3. For catalysts providing poor control of the polymerization process, this value increases to 1.28, 1.3, and 1.45 for T-AMe-SCF_3, T-AMe-CN, T-Pip, respectively, which is related to a strong shift of the peaks toward high molecular weights.

Photochemical Mechanism. *TX-Based Compounds as Electron Donors in Photoinitiator Systems.* Electrochemical properties of thioxanthone derivatives were investigated using cyclic voltammetry, and potentials of oxidation and reduction were determined and summarized in Table 2. Voltammograms for all studied compounds are placed in the Supporting Information (Figures S94−S123). Commercially available and commonly used sensitizers TX and DETX are characterized by high values of oxidation potential (1765 and 1675 mV vs Ag/AgCl, respectively). Modification of 2,4-diethyltioxanthen-9-one and tioxanthen-9-one skeletons by introduction of an amine moiety led to a significant decrease in the values of oxidation potential from ∼1700 to ∼1000 mV. It can be observed that disubstituted thioxanthone derivatives have a lower oxidation potential than the corresponding monosubstituted compound.

For bimolecular initiating systems with investigated compounds and iodonium salt, which are presented in this Article, it is supposed that photoinduction of polymerization

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Table 2. Electrochemical Properties of Derivatives of Thioxanthone

	compound	E_{ox} [c]	E_{red} [d]	E_{S1} [a]	ΔG_{et} [b] vs IOD	ΔG_{et} [b] vs EBPA	K_{SV} [M^{-1}]
series 1	T-A	1038	−1517	3.06	−1.38	−0.76	24.36
	T-AMe	987	−1635	2.59	−0.97	−0.34	68.52
	T-APh	1046	−1587	2.72	−1.03	−0.41	42.95
	T-A-CN	1169	-	2.72	−0.91	−0.29	92.93
	T-AMe-CN	1169	−1555	2.59	−0.78	−0.16	83.95
	T-A-SCF_3	1136	−1599	2.68	−0.91	−0.28	70.54
	T-AMe-SCF_3	1081	−1589	2.65	−0.93	−0.31	24.97
	T-Pip	894	−1660	2.54	−1.01	−0.39	64.74
series 2	T-bisA	961	−1463	2.69	−1.09	−0.47	30.26
	T-bis(AMe)	894	−1573	2.49	−0.96	−0.34	11.87
	T-bis(APh)	961	−1537	2.46	−0.85	−0.24	53.38
	T-bis(A-CN)	1169	-	2.68	−0.87	−0.25	78.55
	T-bis(AMe-CN)	1112	−1453	2.58	−0.83	−0.21	74.23
	T-bis(A-SCF_3)	1045	−1541	2.57	−0.89	−0.26	73.77
	T-bis(AMe-SCF_3)	1073	−1453	2.54	−0.83	−0.21	14.40
	T-bis(Pip)	754	−1691	2.43	−1.03	−0.42	117.05
ref	TX	1765	−1611	3.00	−0.78	−0.17	-
	DETX	1675	−1770	3.19	−0.69	−0.07	-

[a] E_{S1}: energy of singlet state for thioxanthones [eV]. [b] ΔG_{et} values determined from the Rehm−Weller equation [eV]: $\Delta G_{et} = F[E_{ox}\ (D/D^{\bullet+}) - E_{red}(A^{\bullet-}/A)] - E_{S1/T1} - Ze^2/\varepsilon a$. $Ze^2/\varepsilon a$ is negligible in polar solvents. [c] $E_{ox}\ (D/D^{\bullet+})$: oxidation potential of the thioxanthone derivatives measured by cyclic voltammetry vs Ag/AgCl, [mV]. [d] $E_{red}\ (A^{\bullet-}/A)$: reduction potential determined using cyclic voltammetry vs Ag/AgCl, [mV], $E_{red\ IOD}$ = −0.64 V vs Ag/AgCl,[50] $E_{red\ EBPA}$= −1.26 V vs Ag/AgCl.[51]

progresses by an electron-transfer mechanism. Thioxanthone derivatives are used as photosensitizers of the initiator, onium salt. Photosensitization possibilities are dependent on the thermodynamics of the photodriven electron-transfer process. The free energy change of the process, which is stated by the Rehm−Weller equation, was calculated for all studied compounds. The singlet excited state energy (E_{S1}), which is necessary for calculations of the free energy change, was established based on the crossing of the absorption and emission spectra (examples are placed in Supporting Information, Figures S78−S93). Values of ΔG_{et} for the electron-transfer process between thioxanthone derivatives and iodonium salt (IOD) or alkyl bromide (EBPA) are listed in Table 2. All ΔG_{et} values are negative; it can be summarized that electron-transfer processes are feasible. Values of ΔG_{et} vs IOD fluctuate in the range between −1.38 and −0.83 eV, and they are more negative than for DETX/IOD and TX/IOD (ΔG_{et} = −0.69 eV and ΔG_{et} = −0.78 eV). The free energy change vs EBPA oscillates around −0.76 and −0.16 eV. These calculations indicate that processes of the electron transfers in the studied systems are thermodynamically favorable. That is the reason why the generated photoredox pairs should successfully produce active species, which are necessary in the initiation of the photopolymerization processes of monomers.

The addition of IOD to acetonitrile solutions containing thioxanthone derivatives was performed in order to study the interaction between photosensitizers and iodonium salt. This experiment results in strong fluorescence quenching. The Stern−Volmer plot ($I_0/I = 1 + K_{SV}$ [IOD], I_0 and I mean fluorescence intensities for thioxanthone derivative without and with the additive) that was obtained provides linear correlations (figures with fluorescence quenching and the Stern−Volmer plot for all investigated compounds are in the Supporting Information, Figures S50−S77). The Stern−Volmer coefficients (K_{SV}) derived from the slopes of the correlations are in the range of 11−117 M^{-1} as summarized in Table 2. In light-activated atom transfer radical polymerization, bromide (EBPA) is reduced by an electron transfer from the excited state to generate radicals that take part in initiation of polymerization of methyl methacrylate.

CONCLUSION

We have demonstrated that thioxanthone derivatives with absorption properties in the visible range can be easily synthesized in Buchwald−Hartwig coupling. Spectroscopic and electrochemical properties of these compounds were investigated.

Obtained compounds play a role of photosensitizers in two-component photoinitiating systems with iodonium salt in processes induced with LEDs of 420, 455, and 470 nm. These systems were successfully applied for cationic polymerization of epoxy monomer, free-radical polymerization of an acrylate monomer, and also for synthesis of IPN structures. Thioxanthone-based compounds prosperously act in bimolecular photoinitiators with alkyl bromide and in three-component systems in conjunction with bromide and amine for photopolymerization ofan acrylate monomer.

Studied compounds also proved to be efficient photocatalysts in photo-ATRP processes of methyl methacrylate in the presence of alkyl bromide.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.1c00886.

Synthesis of thioxanthen-9-one derivatives, ^1H and ^{13}C NMR spectra, photopolymerization profiles of UVA-CURE1500 and TMPTA, tables with final functional group conversions after photopolymerization processes, fluorescence emission quenching by IOD and Stern−Volmer plots, excitation and emission spectra, cyclic voltammetry results for oxidation and reduction processes, patterns obtained after 3D printing experi-

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ment, description of photochemical reactor for ATRP (PDF)

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Notes

The authors declare no competing financial interest.

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